

Structural distortion and the spin liquid state in $\text{Tb}_2\text{Ti}_2\text{O}_7$

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It is shown that a $\vec{k} = 0$, A_{2u} distortion of the terbium tetrahedral network in $\text{Tb}_2\text{Ti}_2\text{O}_7$ causes the apparent isolation of single tetrahedra as seen in neutron scattering studies. Single tetrahedron collective spin states, rather than individual spins, account for the main features of the spin liquid state, namely, fluctuating local moments and the absence of long range order. Singlet and doublet collective spin ground states are considered. An effective interaction between tetrahedra on the fcc lattice is derived and found to be weak and anisotropic.

PACS numbers: 75.10.Jm, 75.25.+z

$\text{Tb}_2\text{Ti}_2\text{O}_7$ is an example of three dimensional geometric frustration because the magnetic Tb^{3+} ions are arranged on a corner-sharing tetrahedral network. It has a spin liquid phase, characterised by the absence of long range correlations and rapidly fluctuating local magnetic moments, which persists down to at least 50 mK.^{1,2} This article is devoted to another mysterious feature of $\text{Tb}_2\text{Ti}_2\text{O}_7$, namely the apparent isolation of single tetrahedra from the tetrahedral network. Such isolation is suggested by neutron scattering experiments, which find that magnetic correlations beyond the size of a single tetrahedron are absent,¹ and exact calculations of spin eigenstates on single tetrahedra reproduce well diffuse neutron scattering patterns.^{4,5}

A reasonable description of the exchange interaction across the four Tb sites on a single tetrahedron in $\text{Tb}_2\text{Ti}_2\text{O}_7$ has been obtained only recently.^{4,5} The crystal electric field (CEF) ground state of the Tb ions is a doublet, giving rise to a classical picture of Ising-like spins constrained to point into or out of the four vertices of the tetrahedron. However, mixing with higher CEF levels tends to restore transverse spin components, negating the classical picture. The resulting ground state resembles neither the ferromagnetic “spin ice” states, which have two spins pointing inside the tetrahedron and two pointing out, nor the anti-ferromagnetic “all-in or all-out” states. Instead it is a linear combination of various states and with no classical analogue.

The issue of how to deal with the entire tetrahedral network, and why the single tetrahedron picture is valid, remains an outstanding problem. Because of the connectivity of the tetrahedral network, eigenstates of a single tetrahedron are not in general eigenstates of the entire tetrahedral network. This article offers a solution to this paradox, which involves symmetry breaking in the form of a lattice distortion.

Lattice distortions are often invoked in theory as a way to relieve geometrical frustration and arrive at an ordered state,⁶ and usually these involve a change of the crystal system, for example, from cubic to tetragonal. In fact, there is evidence that such a transition occurs in $\text{Tb}_2\text{Ti}_2\text{O}_7$ below any accessible temperature.⁷ In this article, we propose another kind of lattice distortion, one

which lowers the point group symmetry but leaves the crystal system unchanged. This distortion does not remove the frustration completely, but it does serve to isolate single tetrahedra. Collective spin states on single tetrahedra then replace individual spins as the fundamental basis for excitations and longer range effective interactions. The main features of the spin liquid phase follow from this scenario.

Pyrochlore crystals such as $\text{Tb}_2\text{Ti}_2\text{O}_7$ belong to the cubic space group $Fd\bar{3}m$ (O_h^7 , No. 227), in which both Tb and Ti ions form separate, corner-sharing tetrahedral networks. Here we are only concerned with the magnetic Tb^{3+} ions. The tetrahedra appear in two different orientations (A and B), which alternate in the tetrahedral network. A tetrahedron of either type comprises the primitive unit cell. Thus the set of all A tetrahedra form a face-centred cubic (fcc) lattice, as do the set of all B tetrahedra. The set of A tetrahedra are related to the set of B tetrahedra by the π and $\pi/2$ screw rotation and inversion elements of $Fd\bar{3}m$.

We begin by considering the nearest neighbour isotropic (Heisenberg) exchange interaction. The Hamiltonian for the entire tetrahedral network can be split into two terms

$$H_{ex} = \mathcal{J}H_A + \mathcal{J}H_B \quad (1)$$

where \mathcal{J} is the exchange coupling constant,

$$H_A = \sum_k X_{(Ak)} \quad (2)$$

and $X_{(Ak)}$ is the exchange interaction over the k -th A tetrahedron, and H_B is the exchange interaction over the set of B tetrahedra. In either case, the sum over k is a sum over fcc lattice sites. The exchange interaction is

$$X = \sum_{\langle ij \rangle} \vec{J}_i \cdot \vec{J}_j \quad (3)$$

where the sum runs over four sites on a given tetrahedron. The eigenstates of H_A and H_B are known, and are simply the direct products across tetrahedra of the eigenstates for a single tetrahedron, which are given in Ref. 4 and described below. However, in general, $[H_A, H_B] \neq 0$,

therefore H_A and H_B do not have common eigenstates with each other or with H_{ex} (an exception to this is discussed below). This is in apparent contradiction with the results of experiments, which agree very well with the single tetrahedron picture.^{1,4,5} This suggests that H_{ex} (1) should be replaced by an effective Hamiltonian⁸

$$H_{eff} = \mathcal{J}_A H_A + \mathcal{J}_B H_B \quad (4)$$

where one of the couplings is much larger than the other. The difference between the exchange couplings \mathcal{J}_A and \mathcal{J}_B could originate from a structural distortion which makes the A tetrahedra smaller and the B tetrahedra larger, thus $\mathcal{J}_A > \mathcal{J}_B$, or vice versa. Such a distortion is a $\vec{k} = 0$, A_{2u} mode of the Tb ions which reduces the space group symmetry from $Fd\bar{3}m$ to $F43m$.⁹ This new space group is compatible with an otherwise unexplained $(0, 0, 2)$ Bragg peak observed in neutron scattering measurements.¹⁰ If present, domains could produce isolated spins along their boundaries, possibly contributing to observed glassy behaviour.^{2,11,12}

Fits to the dominant $(3, 1, 1)$, $(2, 2, 2)$, $(1, 1, 1)$ and $(2, 2, 0)$ Bragg peaks are in good agreement with the pyrochlore space group $Fd\bar{3}m$.¹⁰ Therefore it is reasonable to assume that the much smaller $(0, 0, 2)$ peak is due to a small distortion of $Fd\bar{3}m$. The space groups which are compatible with all five of the peaks, are cubic, and which are also subgroups of $Fd\bar{3}m$ are $F43m$ (No. 216, T_d^2), $P43m$ (No. 215, T_d^1), $F23$ (No. 196, T^2), $P23$ (No. 195, T^1) and $P2_13$ (No. 198, T^4). Among these, $F43m$ has the highest symmetry, and all are subgroups of $F43m$. Thus it is strongly indicated that the space group of $Tb_2Ti_2O_7$ is in fact $F43m$. The $\vec{k} = 0$, A_{2u} displacement mode which gives rise to $F43m$ can occur for the Tb, Ti or O ions,⁹ although physical considerations point in favour of Tb displacements, as discussed above, or O displacements due to the role that the O ions play in mediating the exchange interaction. Whether or not the $(0, 0, 2)$ peak is present at all temperatures, or appears due to some kind of exotic “spin Jahn-Teller” effect, remains to be investigated.¹⁶

The ratio $\mathcal{J}_A/\mathcal{J}_B$ varies with the size of the lattice distortion. The localised nature of the Tb $4f$ electrons ensures that overlap integrals contributing to the exchange constants will be very sensitive to changes in relative distances, and this is evidenced by very large magnetostriction.¹³ Therefore it is possible that even a very small lattice distortion could produce a large difference between \mathcal{J}_A and \mathcal{J}_B .

Assuming that $|\mathcal{J}_A| > |\mathcal{J}_B|$, we will find the ground state of H_A and then consider H_B as a perturbation. In order to do this, we must first describe the collective spin states of a single tetrahedron. A tetrahedron has four magnetic ions at its vertices, each of which has a local site symmetry of D_{3d} . Following the conventions established in Ref. 4, we label the ions #1, 2, 3 and 4, where their C_3 axes point in the directions $[1, 1, 1]$, $[-1, -1, 1]$, $[-1, 1, -1]$ and $[1, -1, -1]$ respectively. Tb^{3+}

ions have a total angular momentum of $J = 6$, but the 13-fold degeneracy is split by the crystal electric field into 5 singlets and 4 doublets; one of the doublets is the ground state. We take the ground state as¹⁴ $|\pm\rangle = \pm 0.13|\pm 5\rangle \mp 0.13|\mp 1\rangle - 0.95|\mp 4\rangle$, where the quantisation axis points in the direction of the C_3 axis for each Tb ion. There are then 16 collective spin states on a tetrahedron, which can be written as $|\pm\pm\pm\pm\rangle = |\pm\rangle_1 \otimes |\pm\rangle_2 \otimes |\pm\rangle_3 \otimes |\pm\rangle_4$, where the subscripts indicate the site on the tetrahedron. Symmetry considerations predict that interactions will split the 16 states into a singlet, three doublets and three triplets,⁴ which are complicated linear combinations of the basis states $|\pm\pm\pm\pm\rangle$.

The ground state spin configuration of Tb ions on a single tetrahedron for isotropic anti-ferromagnetic exchange is a doublet,⁴ which we write as $|E_{\pm}\rangle$. Otherwise the ground state depends on the details of the anisotropy. An anisotropic interaction (equivalent to including nearest neighbour dipole-dipole interactions) was considered in Ref. 5 and the singlet was found to be the ground state. A triplet ground state could also yield patterns similar to what are found in experiment.⁴ In the following, we will consider the doublet and the singlet as possible ground states on a single tetrahedron.

The ground state of H_A is constructed by taking the direct product of the single tetrahedron ground states across the A tetrahedra. If the tetrahedron ground state is the singlet,

$$|A_1\rangle = (|++--\rangle + |--++\rangle + |+-+-\rangle + |-+-+\rangle + |-++-\rangle + |--+-\rangle)/\sqrt{6} \quad (5)$$

then the ground state of H_A can be written $\Pi_k |A_1\rangle_k$, where k indexes tetrahedra, that is, fcc lattice sites. This state clearly has long range correlations but they will be undetectable in static neutron scattering measurements, in agreement with experiment.¹ This is because neutron scattering detects magnetic correlations, which are proportional to the matrix elements $\langle\Psi|\vec{J}_i|\Phi\rangle\langle\Phi|\vec{J}_j|\Psi\rangle$, where i and j are Tb sites and Ψ and Φ are eigenstates of H_A , which vanish unless i and j belong to the same A tetrahedron. On the other hand, higher order correlations, beginning with quadrupolar, will exist between tetrahedra. Thus the state $\Pi_k |A_1\rangle_k$ is not a true spin liquid. The excitation spectrum of H_A will be gapped, with an energy of the order of $0.1 \sim 1$ K,⁵ corresponding to the separation between $|A_1\rangle$ and the first excited state on the tetrahedron.

If the tetrahedron ground state is a doublet $|E_{\pm}\rangle$ then the ground states of H_A can be written as $\prod_k |E_{\sigma}\rangle_k$. The ground state is highly degenerate. One way of viewing the degeneracy is to note that the state at each site can be any complex linear combination of the doublet states $|E_{\pm}\rangle$. This $SU(2)$ freedom on each fcc site leads to the absence of correlations of any kind beyond the size of a single tetrahedron. However, interactions coming from the perturbation H_B will limit this freedom. Ultimately, we find a system of weakly interacting tetrahedra

arranged on an fcc lattice (which is also frustrated). If the tetrahedron ground state is a triplet then there will be a SU(3) symmetry on each lattice site, which could also be limited by weak interactions.

In order to calculate the effect of the perturbation H_B we first need to examine in detail the exchange interaction over a single tetrahedron and its eigenstates. A useful representation of the exchange interaction over a single tetrahedron is given in Ref. 4 in which the angular momentum operators are expressed in terms of local coordinate axes (indicated by subscripts) such that the local z axis for each Tb ion points in the direction of its C_3 axis. Local x and y axes have also been implicitly selected. The result is written in Table I. Only local coordinate operators are used in the following. The symmetry of the crystal is octahedral, which permits three separate invariant terms in the exchange interaction, $\mathcal{J}_1 X_1$, $\mathcal{J}_2 X_2$ and $\mathcal{J}_3 X_3$, where $\mathcal{J}_{1,2,3}$ are different exchange couplings for each term, and $X_{1,2,3}$ are the sums of all the terms in the second, third and fourth columns respectively of Table I. There is actually a fourth invariant allowed under O_h symmetry (X_3 is split), which we do not consider here, although the following discussion can be easily generalised. The isotropic exchange interaction is the sum of all three terms with $\mathcal{J}_1 = \mathcal{J}_2 = \mathcal{J}_3$. In the following, we will assume that the exchange interaction is antiferromagnetic.

The matrix elements for $J_{z,\pm}$ are

$$\langle \pm | J_z | \pm \rangle = \pm j \quad (6)$$

$$\langle \pm | J_{\pm} | \mp \rangle = t \quad (7)$$

The parameters j and t serve as a very useful characterisation of single-ion doublet spin states. For $J = 1/2$ ions, $j = 1/2$ and $t = 1$, while for other $1/2$ -integral spins j and t may be quite different. The parameter t equals zero for integral spins (as for the Tb^{3+} ion) but may acquire a significant non-zero value due to mixing with higher crystal electric field levels.⁵ A comparison between theoretical and experimental diffuse neutron scattering patterns suggests that t is larger than j in $\text{Tb}_2\text{Ti}_2\text{O}_7$.^{4,5} Thus, in our initial approximation, we will assume that $j = 0$; then only term in the exchange interaction with non-zero matrix elements is X_3 .

The ground state of X_3 is the doublet^{4,15}

$$|E_{\pm}\rangle = \sqrt{3/5}|E_{\pm}^{(1)}\rangle - \sqrt{2/5}|E_{\pm}^{(3)}\rangle \quad (8)$$

where

$$|E_+^{(1)}\rangle = |++++\rangle, \quad |E_-^{(1)}\rangle = |----\rangle \quad (9)$$

$$|E_+^{(3)}\rangle = (|++--\rangle + \varepsilon|+-+-\rangle + \varepsilon^2|+--+ \rangle + |--++\rangle + \varepsilon|-+-+\rangle + \varepsilon^2| -++-\rangle)/\sqrt{6} \quad (10)$$

$$|E_-^{(3)}\rangle = [|E_+^{(3)}\rangle]^* \quad (11)$$

where $\varepsilon = \exp \frac{2i\pi}{3}$. First order corrections due to H_B are found by calculating the matrix elements of H_B between

the degenerate ground states of H_A . We will express the final result as an effective interaction between the ground state doublets on neighbouring tetrahedra. Recall that H_B is the exchange interaction summed over all B tetrahedra. It consists of terms of the form $\vec{J}_i \cdot \vec{J}_j$, where i and j are nearest neighbour but are found on different, neighbouring A tetrahedra. Nearest neighbour A tetrahedra share exactly one pair of nearest neighbour magnetic ions. Considering only the X_3 part of the exchange interaction, we find that *all* of the ground state matrix elements vanish¹⁷ because each term in H_B raises or lowers at most one site in any A tetrahedron, and the result is orthogonal to all of the ground states. Therefore, to first order in $\mathcal{J}_B/\mathcal{J}_A$ and zeroth order in j/t , the A tetrahedra are non-interacting.

Now we consider finite values of j/t by including X_1 and X_2 in the exchange interaction. This will add mixtures of

$$|E_+^{(2)}\rangle = (|+- --\rangle + |-+- -\rangle + |- - - +\rangle + |- - - +\rangle)/2 \quad (12)$$

$$|E_-^{(2)}\rangle = (|-++ ++\rangle + |+- ++\rangle + |++ - +\rangle + |++ - +\rangle)/2 \quad (13)$$

and

$$|E_{\pm}^{(3')}\rangle = \sqrt{2/5}|E_{\pm}^{(1)}\rangle + \sqrt{3/5}|E_{\pm}^{(3)}\rangle \quad (14)$$

to $|E_{\pm}\rangle$. The general form is $|E_{\pm}\rangle = \alpha|E_{\pm}^{(1)}\rangle + \beta|E_{\pm}^{(2)}\rangle + \delta|E_{\pm}^{(3)}\rangle$. To find the effective interaction between tetrahedra, consider two neighbouring A tetrahedra, with Tb sites numbering 1, 2, 3, and 4 on the first tetrahedron and 5, 6, 7 and 8 on the second. Projecting all possible ground states of H_A onto the subspace of these two tetrahedra yields four states of the form $|E_{\pm}; E_{\pm}\rangle$. Suppose that sites 1 and 6 are nearest neighbours and that the C_3 axis of site 6 points in the same direction as that of site 2. Then $\vec{J}_1 \cdot \vec{J}_6$ is a term in H_B and takes the same form as $\vec{J}_1 \cdot \vec{J}_2$. The effective interaction between tetrahedra is found by calculating the 16 matrix elements $\langle E_{\pm}; E_{\pm} | \vec{J}_1 \cdot \vec{J}_6 | E_{\pm}; E_{\pm} \rangle$. The non-zero matrix elements are

$$\begin{aligned} \langle E_+; E_{\pm} | X_1 | E_+; E_{\pm} \rangle &= \langle E_-; E_{\mp} | X_1 | E_-; E_{\mp} \rangle = \mp \gamma^2/3 \\ \langle E_+; E_{\pm} | X_2 | E_+; E_{\mp} \rangle &= \langle E_{\pm}; E_+ | X_2 | E_{\mp}; E_+ \rangle = -\gamma\tau\sqrt{2}/3 \\ \langle E_-; E_{\pm} | X_2 | E_-; E_{\mp} \rangle &= \langle E_{\pm}; E_- | X_2 | E_{\mp}; E_- \rangle = \gamma\tau\sqrt{2}/3 \\ \langle E_+; E_+ | X_3 | E_-; E_- \rangle &= \langle E_-; E_- | X_3 | E_+; E_+ \rangle = \tau^2/3 \\ \langle E_+; E_- | X_3 | E_-; E_+ \rangle &= \langle E_-; E_+ | X_3 | E_+; E_- \rangle = -\tau^2/6 \end{aligned}$$

where $\gamma = j(\alpha^2 - \beta^2/2)$ and $\tau = t\alpha\beta$. From these matrix elements we can infer that the effective interaction between tetrahedra is anisotropic in general and can be divided into three separate terms

$$H_{tetra} = \mathcal{J}'_1 X_1 + \mathcal{J}'_2 X_2 + \mathcal{J}'_3 X_3, \quad (15)$$

where X_i now operate on tetrahedral ground state doublets, as follows. There are four invariant operators on

term	X_1	X_2	X_3	bond
$\vec{J}_1 \cdot \vec{J}_2$	$-\frac{1}{3}J_{1z}J_{2z}$	$-\frac{\sqrt{2}}{3}[J_{1z}(J_{2+} + J_{2-}) + (J_{1+} + J_{1-})J_{2z}]$	$\frac{1}{3}(J_{1+}J_{2+} + J_{1-}J_{2-}) - \frac{1}{6}(J_{1+}J_{2-} + J_{1-}J_{2+})$	$(1/2, 1/2, 0)$
$\vec{J}_3 \cdot \vec{J}_4$	$-\frac{1}{3}J_{3z}J_{4z}$	$-\frac{\sqrt{2}}{3}[J_{3z}(J_{4+} + J_{4-}) + (J_{3+} + J_{3-})J_{4z}]$	$\frac{1}{3}(J_{3+}J_{4+} + J_{3-}J_{4-}) - \frac{1}{6}(J_{3+}J_{4-} + J_{3-}J_{4+})$	$(-1/2, 1, 2, 0)$
$\vec{J}_1 \cdot \vec{J}_3$	$-\frac{1}{3}J_{1z}J_{3z}$	$-\frac{\sqrt{2}}{3}[J_{1z}(\varepsilon J_{3+} + \varepsilon^2 J_{3-}) + (\varepsilon J_{1+} + \varepsilon^2 J_{1-})J_{3z}]$	$\frac{1}{3}(\varepsilon^2 J_{1+}J_{3+} + \varepsilon J_{1-}J_{3-}) - \frac{1}{6}(J_{1+}J_{3-} + J_{1-}J_{3+})$	$(1/2, 0, 1/2)$
$\vec{J}_2 \cdot \vec{J}_4$	$-\frac{1}{3}J_{2z}J_{4z}$	$-\frac{\sqrt{2}}{3}[J_{2z}(\varepsilon J_{4+} + \varepsilon^2 J_{4-}) + (\varepsilon J_{2+} + \varepsilon^2 J_{2-})J_{4z}]$	$\frac{1}{3}(\varepsilon^2 J_{2+}J_{4+} + \varepsilon J_{2-}J_{4-}) - \frac{1}{6}(J_{2+}J_{4-} + J_{2-}J_{4+})$	$(-1/2, 0, 1/2)$
$\vec{J}_1 \cdot \vec{J}_4$	$-\frac{1}{3}J_{1z}J_{4z}$	$-\frac{\sqrt{2}}{3}[J_{1z}(\varepsilon^2 J_{4+} + \varepsilon J_{4-}) + (\varepsilon^2 J_{1+} + \varepsilon J_{1-})J_{4z}]$	$\frac{1}{3}(\varepsilon J_{1+}J_{4+} + \varepsilon^2 J_{1-}J_{4-}) - \frac{1}{6}(J_{1+}J_{4-} + J_{1-}J_{4+})$	$(0, 1/2, 1/2)$
$\vec{J}_2 \cdot \vec{J}_3$	$-\frac{1}{3}J_{2z}J_{3z}$	$-\frac{\sqrt{2}}{3}[J_{2z}(\varepsilon^2 J_{3+} + \varepsilon J_{3-}) + (\varepsilon^2 J_{2+} + \varepsilon J_{2-})J_{3z}]$	$\frac{1}{3}(\varepsilon J_{2+}J_{3+} + \varepsilon^2 J_{2-}J_{3-}) - \frac{1}{6}(J_{2+}J_{3-} + J_{2-}J_{3+})$	$(0, -1/2, 1/2)$

TABLE I: The exchange interaction over a single tetrahedron expressed in terms of local coordinates for each Tb ion. The first column lists the terms in the exchange interaction over a single tetrahedron. In each row, the first entry is the sum of the middle three. The isotropic exchange is the sum of all the terms in the middle three columns, and may be divided into three anisotropic terms X_1 , X_2 and X_3 which are sum of all the terms in each of the middle three columns. The last column lists the bond direction for each term. $\varepsilon = \exp \frac{2i\pi}{3}$.

the fcc lattice that are directly related to the four invariants on the single tetrahedron (note that, as explained above, only three have been considered here). The bond direction between a tetrahedron and each of its twelve nearest neighbours can be defined by the bond direction between the nearest neighbour ion sites on neighbouring tetrahedra. Six different bond directions are present. The bond direction determines the correspondence between rows in Table I and terms in the effective interaction between tetrahedra. Assuming that matrix elements of the tetrahedron operators are $\langle E_{\pm} | J_z | E_{\pm} \rangle = \pm 1$ and $\langle E_{\pm} | J_{\pm} | E_{\mp} \rangle = 1$, we find $\mathcal{J}'_1 = \mathcal{J}_1 \gamma^2$, $\mathcal{J}'_2 = \mathcal{J}_2 \gamma \tau$ and $\mathcal{J}'_3 = \mathcal{J}_3 \tau^2$. Higher order corrections arising from mix-

ing via H_B between the single tetrahedron ground states $|E_{\pm}\rangle$ and excited states will further renormalise \mathcal{J}'_1 , \mathcal{J}'_2 and \mathcal{J}'_3 . The renormalisation of the coupling constants in Eq. 15 implies that even if the underlying exchange interaction is isotropic, the effective exchange interaction between tetrahedra is anisotropic. In a similar fashion, the effective interaction between tetrahedra with triply degenerate ground states can also be found.

Anisotropy in H_{tetra} may assist long range ordering of the tetrahedra. However, at temperatures so far obtained, there is no evidence from neutron scattering for any kind of inter-tetrahedra correlations. The inelastic neutron scattering function is proportional to¹⁹

$$I(\mathbf{q}) \propto \sum_m e^{-E_m/k_B T} \sum_{i,j} \sum_{a,b} \sum_n (\delta^{ij} - \hat{q}^i \hat{q}^j) \langle m | J_a^i | n \rangle \langle n | J_b^j | m \rangle e^{i\mathbf{q} \cdot (\mathbf{r}_b - \mathbf{r}_a)}, \quad (16)$$

where a and b are the four magnetic ion sites at the corners of a tetrahedron and n and m are eigenstates of the system. The angular momentum operators J^i refer to the global coordinate system (indicated by superscripts). This formula yields patterns which are linear combinations of the following functions

$$f^1(h, k, l) = \frac{1}{h^2 + k^2 + l^2} \left[hk \sin \frac{\pi h}{2} \sin \frac{\pi k}{2} + kl \sin \frac{\pi k}{2} \sin \frac{\pi l}{2} + hl \sin \frac{\pi h}{2} \sin \frac{\pi l}{2} \right] \quad (17)$$

$$f^2(h, k, l) = \frac{1}{h^2 + k^2 + l^2} \left[h^2 \cos \frac{\pi k}{2} \cos \frac{\pi l}{2} + k^2 \cos \frac{\pi h}{2} \cos \frac{\pi l}{2} + l^2 \cos \frac{\pi h}{2} \cos \frac{\pi k}{2} \right] \quad (18)$$

$$f^3(h, k, l) = \frac{1}{h^2 + k^2 + l^2} \left[h^2 \cos \frac{\pi h}{2} \left(\cos \frac{\pi k}{2} + \cos \frac{\pi l}{2} \right) + k^2 \cos \frac{\pi k}{2} \left(\cos \frac{\pi h}{2} + \cos \frac{\pi l}{2} \right) + l^2 \cos \frac{\pi l}{2} \left(\cos \frac{\pi h}{2} + \cos \frac{\pi k}{2} \right) \right] \quad (19)$$

Inter-tetrahedron correlations would be manifested in the appearance of smaller period (in k space) contributions to the scattering patterns. If present, these could help to constrain the effective interaction between tetrahedra. However, their absence indicates that inter-tetrahedra interactions are indeed weak.

Finally, let us contrast our results to situations in which the commutator $[H_A, H_B]$ does vanish, allowing common eigenstates of H_A , H_B and H_{ex} . Non-zero terms

in the commutator $[H_A, H_B]$ arise from terms proportional to X_2 and X_3 in H_A and H_B . Thus, if the exchange interaction is highly anisotropic and only X_1 appears or when the parameter t vanishes, then $[H_A, H_B] = 0$, and the eigenstates of H , H_A or H_B are the sixteen basis states $|\pm \pm \pm \pm\rangle$. If the sign of \mathcal{J}_1 is positive then the ground states of a single tetrahedron are the antiferromagnetic states $|+++-\rangle$ and $|- - - -\rangle$; otherwise the ground state has a six fold degeneracy, $|++--\rangle$,

$|--++\rangle, |+-+-\rangle, |-+-+\rangle, |+-+-\rangle$ and $|-++-\rangle$. These situations can each be defined by rules: “all in or all out” in the former and “two in/two out” (spin ice rule) in the latter. Ground states of H_A are again found by taking the direct product of ground states over the A tetrahedra. A ground state of H_A will be an eigenstate of H_B but in general it will not be a ground state unless the appropriate ground state rule is satisfied on all of the B tetrahedra too. The distinguishing feature between the special case when $[H_A, H_B] = 0$ and the general case is the form that the eigenstates take. When the commutator is non-zero the eigenstates of the single tetrahedron are necessarily entangled, that is, they must be linear combinations of the basis states $|\pm\pm\pm\pm\rangle$, which leads to fluctuating local moments found in $\text{Tb}_2\text{Ti}_2\text{O}_7$.

To summarise, we have shown that a $\vec{k} = 0$, A_{2u} lattice distortion can account for the observed single tetrahedron behaviour. This distortion results in a space group of

$F\bar{4}3m$, which is compatible with with a $(0,0,2)$ Bragg peak observed by neutron scattering¹⁰ and the loss of inversion centre recently observed in Raman scattering.²⁰ The eigenstates of the system are then direct products over the fcc lattice of the single tetrahedron eigenstates. The effective interaction between tetrahedra is weak and anisotropic.

Acknowledgments

I thank E. Altman and M. Gingras for very helpful discussions. I am very grateful to the Department of Condensed Matter Physics at the Weizmann Institute of Science, especially A. Finkel'stein, for hospitality and support while this work was being completed, and also to the Shrum Foundation and NSERC for support.

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